ELECTROMETRIC DETERMINATION OF ALDEHYDES AND KETONES

BY

GARRARD ERNEST ALFRED WYLD

B.A., Reed College, 1941
M.S., State University of Iowa, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ELECTROMETRIC DETERMINATION OF ALDEHYDES AND KETONES

BY

GARRARD ERNEST ALFRED WYLD

B.A., Reed College, 1941
M.S., State University of Iowa, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1949

URBANA, ILLINOIS

1949

ACKNOWLEDGMENT

The author wishes to express his thanks to Dr. G. L. Clark under whose direction this work was undertaken. He also wishes to thank Dr. R. B. Fischer for his help with the electronic problems, Dr. H. A. Laitinen for advice on the theoretical aspects and Dr. R. L. Frank for advice on the purification of the organic compounds. He is especially grateful to his wife, Mary, for her constant help and encouragement.

R. UNIV. BIBLIOTHEEK LEIDEN

PART I

POTENTIOMETRIC DETERMINATION OF ALDEHYDES AND KETONES

Introduction

Numerous workers have described the use of hydroxylamine hydrochloride for the determination of aldehydes and ketones. The formation of an oxime molecule releases a proton from a hydroxylammonium ion, and the acid produced is then titrated with standard base.

Bryant and Smith (1) developed a modification of this method in which pyridine was added to the reaction mixture to prevent its becoming too strongly acid during the oxime formation. This is said to have a favorable effect on the oxime equilibrium of certain hindered ketones. It also renders the initial reaction mixture neutral to bromophenol blue indicator, thus eliminating the need for a blank titration.

These methods have the disadvantage that the endpoints are not sharp and that they cannot be carried out with colored solutions. The addition of pyridine makes the endpoint especially poor because of its buffering action.

Experimental And Results

A potentiometric study of the determination of vanillin showed that pyridine buffered the solution to such an extent that no inflection at all was present in the titration curve at the equivalence point. Furthermore, the point at which the pH meter reading of the sample matched that of the blank did not correspond to the point at which the indicator colors matched.

Without pyridine a fairly good inflection in the titration curve was obtained. However, the bromophenol blue indicator changed color at a pH meter reading considerably above the

steepest part of the curve. A number of other indicators were tested and although none were completely satisfactory, dibromodichlorophenolsulfonphthalein was judged to be somewhat better than bromophenol blue.

It was thought that the use of acetic acid as a solvent would cause hydroxylamine to act as a strong base and thereby give a better titration curve than was obtained in alcohol. Hydroxylammonium acetate was used as the reagent and the excess titrated with perchloric acid in acetic acid. Actually a very poor inflection was obtained under these conditions. However, a mixed solvent of dioxane and acetic acid gave a fairly good inflection. The size of the inflection was limited by the basic strength of the oximes which was appreciable both in acetic acid and in dioxane-acetic acid. In general, the oximes of aliphatic ketones are more basic than those of aldehydes and aromatic ketones.

The reaction rates of various compounds with hydroxylamine in this solvent were found to be similar to those in alcohol. Salicylaldehyde, however, reacted more rapidly in dioxane-acetic acid.

A potentiometric method was developed using dioxane-acetic acid for the determination of aldehydes and ketones. A standard deviation of $\pm$ 0.2 percent was obtained for aldehydes and aromatic ketones and $\pm$ 0.5 percent for aliphatic ketones. The presence of 5.0 g. of benzoic acid in the determination of 0.3 g. of benzaldehyde had no effect on the shape or position of the titration curve in dioxane-acetic acid. The Bryant and Smith method could not be used with benzoic acid present. The alcoholic potentiometric method without pyridine could be used with some loss in precision but the bromophenol blue indicator was useless.

PART II

DIOXANE-ACETIC ACID AS A SOLVENT FOR THE TITRATION OF WEAK BASES

Introduction

Glacial acetic acid has been used extensively (3,8) for the titration of organic bases which are relatively weak in an aqueous system. In part I it was shown that the addition of dioxane has a marked effect on the relative basic strength of hydroxylamine. This effect was studied further with a number of other basic compounds.

Experimental And Results

The applicability of the pH meter and glass electrode to measurements in non-aqueous media (2, 6) is discussed with particular reference to the behavior in glacial acetic acid and dioxane-acetic acid. The pH meter reading at the midpoint of a titration is considered to be a practical measurement of the relative strength of the acid or base being titrated.

The effect of dioxane, benzene, and carbon tetrachloride on the relative basicity of an aliphatic amine in acetic acid was studied. All three increase the basicity of the amine but dioxane caused a much greater increase than the other two. The hydrogen bond-forming ability of dioxane is discussed as a possible reason for its greater influence.

The basic strength of thirty-one compounds relative to perchloric acid was determined in acetic acid and in dioxane-acetic acid. Dioxane causes most of the compounds to appear more basic, but aniline and methylaniline are negligibly affected, while the chloro- and nitroanilines and diphenylamine are made less basic. This behavior is thought to depend upon the dielectric constant of the solvent and the dipole moment of the substituent groups (5, 9, 10, 11).

The use of dioxane-acetic acid as a solvent increases the

precision of titrations of many basic compounds and makes possible the differentiation of certain mixtures of amines which is not possible in acetic acid alone.

PART III

HIGH FREQUENCY OSCILLATORS FOR ELECTROMETRIC TITRATIONS IN INERT SOLVENTS

Introduction

A new type of electrometric titration using a high frequency oscillator which is applicable to essentially non-conducting solutions has recently been introduced by Jensen and Parrack (4). The plate current of the oscillator was a function of the conductance or dielectric constant of a solution placed inside the coil of the plate circuit. Changes in plate current were read very accurately upon a microammeter in a balancing arrangement.

Experimental And Results

The apparatus described by Jensen and Parrack was built and tested. It was found to be sufficiently sensitive for dielectric constant titrations but the oscillator current was too variable for practical use. Attempts to make the current more constant were without success. The oscillator current was found to vary with the logarithm of the dielectric constant of a liquid placed within the coil of the plate circuit.

A commercially available oscillator, the Thermocap relay (7), was tested and found to be very sensitive and stable. Its possibilities as a titration instrument are considered. The controls supplied with the instrument were too crude for practical use. However, with suitable modifications it is believed that the instrument could be used for dielectric constant titrations.

BIBLIOGRAPHY

1. Bryant, W. M. D. and Smith, D. M., J. Am. Chem. Soc. *57*, 57 (1935).

2. Dole, M. "The Glass Electrode", Wiley, New York, 1941.

3. Hall, N. F. and Werner, T. H., J. Am. Chem. Soc., *50*, 2367 (1928).

4. Jensen, F. W. and Parrack, A. L., Ind. Eng. Chem., Anal. Ed. *18*, 595 (1946).

5. Kilpatrick, M., Chem. Rev. *30*, 159 (1942).

6. Lykken, L., Am. Soc. Testing Materials, Symposium on pH Measurements, Tech. Pub. No. 73, 71-9 (1946).

7. Müller, R. H., Ind. Eng. Chem., Anal. Ed. *19*, 21A, Oct. 1947.

8. Nadeau, G. F. and Branchen, L. E., J. Am. Chem. Soc., *57*, 1363 (1935).

9. Schwarzenbach, G. and Egli, H., Helv. Chim. Acta *17*, 1176, 1183 (1934).

10. Wooten, L. A. and Hammett, L. P., J. Am. Chem. Soc., *57*, 2289 (1935).

11. Wynne-Jones, W. F. K., Proc. Roy. Soc. *A140*, 440 (1933).

VITA

The author was born in Portland, Oregon on February 6, 1920, and attended public schools in that city, graduating from Washington High School in June, 1937. He attended Reed College in Portland from 1937 to 1941 when he obtained the Bachelor of Arts degree.

He entered the Graduate School of the State University of Iowa in 1941 where he was a teaching assistant in analytical chemistry, and obtained the Master of Science degree in 1942.

The author was employed as an analyst by the Aluminum Company of America at Vancouver, Washington during the summer of 1942. In 1943 he joined the analytical division of Shell Development Company where he was employed until 1946. In January 1946 he married Mary Elizabeth Batey.

He entered the Graduate School of the University of Illinois in 1946 where he was also a teaching assistant in the analytical division.

He is a member of the American Chemical Society, Sigma Xi, Alpha Chi Sigma, and Phi Lambda Ussilon.

He has published the following paper: "The Determination of Metals in Lubricating Oils", Petroleum Refiner, October, 1945 (with L. Lykken, K. R. Fitzsimmons, and S. A. Tibbetts).